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Emission of Diffuse Bands of Sodium behind Shock Fronts*

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WURM[1] has described a continuous emission band extending from 5490 A to the D lines and inferred the existence of van der Waals states of Na_2. Hamada[2] has classified sodium bands in the red and yellow regions into three groups, *viz.*, (1) red bands (λλ8150–5500), (2) cathode ray fluorescence band, and (3) the continuous band (λλ5470–7200). Recently, wide diffuse bands have been observed and discussed qualitatively for rubidium-rare gas mixtures.[3,4]

By utilizing the shock tube, we have observed the emission of a continuous band corresponding to Hamada's type (3) band. We used finely ground salts as a source of sodium in a one-inch diameter tube; the low-pressure section was 51 in. long and the high-pressure section had a length of 24 in. Mylar diaphragms (0.003 and 0.005 in. thick) separated the two sections. Observations were made through a lucite block at the end of the low pressure section. Spectrograms were taken with a 1.5-m ARL spectrograph with a dispersion of 6.8 A/mm. Kodak Royal-X panchromatic sheet film and Kodak Tri-X panchromatic roll film were used. Intensity measurements were made with an ARL 2250 densitometer.

Measured quantities (from 5 to 300 mg) of finely ground sodium salts (e.g., NaCl, NaBr, and Na_2CO_3) were placed in the Lucite block and spread evenly. Argon, at pressures from 5 to 100 mm Hg, was admitted to the low-pressure section. The high-pressure section was filled with helium and a magnetic breaker used to burst the diaphragm.

We observed atomic lines of Na and a continuous band under various shock conditions. As the amount of sodium salt is increased at constant shock conditions, the D lines become stronger, wider and self-reversed; also the diffuse series lines (λλ5682, 5688) and sharp series lines (λλ6154, 6160) appear. When the quantity of sodium chloride exceeds about 10 mg, the diffuse band becomes superimposed on the atomic lines. Further increases in the amount of sodium chloride up to 300 mg did not change the general features of the spectrum. A typical intensity profile (Fig. 1) shows a continuous band starting at about 5490 A and extending beyond 6200 A. The quantities T_5 and p_5 were estimated by using ideal, one-dimensional shock theory.[5] An intermediate maximum occurs at about 5500 A; on the long-wavelength side the intensity decreases continuously without distinct cutoff.

There is little doubt that the continuous band λλ5490–6200 is identical with Hamada's (3) band and Wurm's band. The discrepancy in the long-wavelength

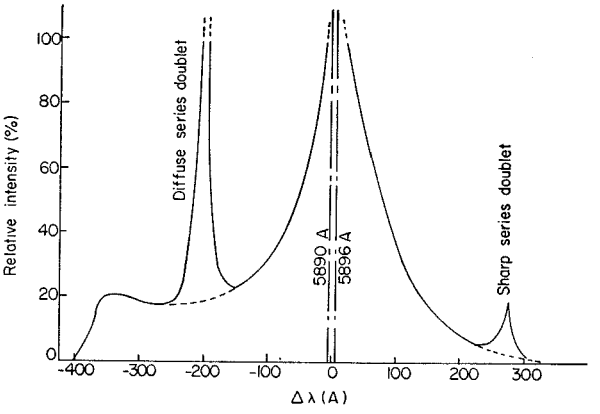

FIG. 1. Intensity distribution of band accompanying D lines; $p_1=50$ mm Hg, $p_4=395$ psi, $p_5=12$ atmos, $T_5=6300°K$, NaCl=50 mg.

extent of the band between Hamada's results and ours may be attributed to the extreme difference of excitation conditions. The principal support for the assertion that the band belongs to Na_2 molecular states comes from the observation that the emission spectrum is independent of the nature of the foreign gas. Wurm considered the structure in the long-wavelength region of the D lines to result from absorption of the red band of Na_2, the background being the broadening of the D lines. On the other hand, Hamada interpreted the entire continuum (both sides of the D lines) to constitute a single band caused by the same mechanism described by Wurm. Recently, Ch'en, Bennett, and Jefimenko[3] have presented potential curves that are consistent with both the red and violet bands. It appears reasonable to conclude that the continuous band results from a transition between a molecular state composed of ^2S and ^2P Na atoms and a similar molecule composed of two ground state Na atoms. It should be noted that Na_2 molecules should be formed behind shock fronts after interaction between the incident or reflected shocks and the rarefaction wave.

Further research of a more quantitative nature is now in progress and will be reported in the near future.

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[1] K. Wurm, Z. Physik **79,** 736 (1932).
[2] H. Hamada, Phil. Mag. **15,** (7), 574 (1933).
[3] Ch'en, Bennett, and Jefimenko, J. Opt. Soc. Am. **46,** 182 (1956).
[4] O. Jefimenko and W. Curtis, J. Chem. Phys. **27,** 953 (1957).
[5] Ressler, Lin, and Kantrowitz, J. Appl. Phys. **23,** 1390 (1952).